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The Use of silica and alumina to catalyze the addition of hydrogen chloride to alkenes

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The Use of Silica Gel and Alumina to Catalyze the Addition of Hydrogen Chloride to Alkenes

By

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THESIS

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ABSTRACT

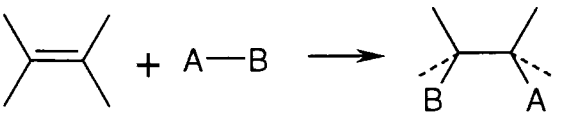
The use of pre-heated silica gel and alumina along with a chlorinating agent, generates HCl *in situ*, which has been found to add to norbornadiene (**IX**). Treated in this fashion, norbornadiene readily results in the formation of two isomers, *exo*-5-chloronorbornene (**XI**) and 3-chloronotricyclene (**XII**) at room temperature in methylene chloride, with *exo*-5-chloronorbornene being the predominant product (70% ± 1%). In promoting the hydrohalogenation reaction, silica gel was found to be less efficient compared to alumina, but undesired diadducts appeared to be less prominent when silica gel rather than alumina was used. Deuterated alumina and thionyl chloride in methylene chloride solution was found to result in the addition of DCl to norbornadiene. Three deuterated products: 29% *exo,exo*-6-chlorobicyclo[2.2.1]hept-2-ene-5-d (**XVII**), 14% *exo,syn*-5-chlorobicyclo[2.2.1]hept-2-ene-7-d (**XVIIa**) and 19% 5-chlorotricyclo[2.2.1.$0^{2,6}$]heptane-3-d (**XVIII**), as well as the two undeuterated products, 27% *exo*-5-chloronorbornene (**XI**) and 11% 3-chloronotricyclene (**XII**), were detected by GC/MS analysis. A higher ratio of **XVII/XVIIa** for the catalyzed DCl addition over the uncatalyzed addition suggests that the surface of the alumina somewhat slowed Wagner-Meerwein rearrangement during this reaction.

INTRODUCTION

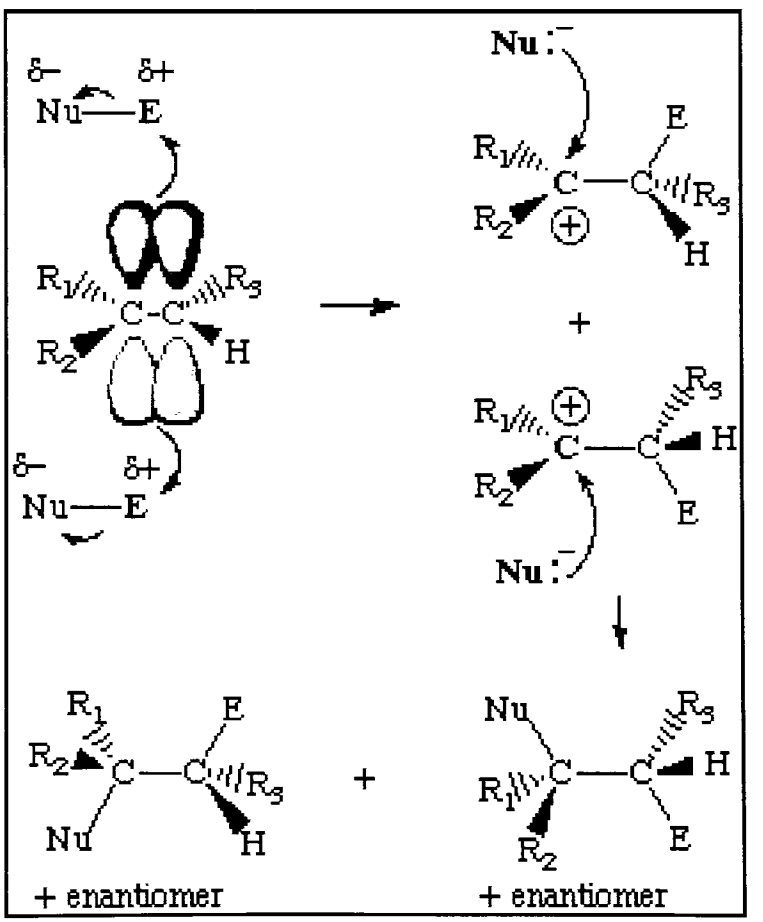
A characteristic reaction of the carbon-carbon double bond of alkenes is an addition reaction of the general type shown below (**Scheme I**). A specific example of this addition is hydrohalogenation. There are two mechanisms possible for hydrohalogenation: one is an ionic process, and the other is a radical process. The ionic process involves the initial attack of a double bond by the electrophilic proton (H^+) of a hydrogen halide (**Scheme II**, $E^+ = H^+$, $Nu^- =$ halide). Using hydrochlorination as an example, a proton will be attracted to the π-electrons of the alkene and will bond such that the more, or most, stable carbocation is produced. The carbocation then traps chloride ion to give the Markovnikov product. Radical addition involves the formation of a carbon radical, induced by, for example, peroxides formed from dissolved oxygen in reagents. The oxygen is able to abstract a hydrogen atom from an organic molecule to form peroxide and a carbon radical, which subsequently initiates the radical addition leading to a predominance of *anti*-Markovnikov product. For example, The addition of HBr to1-octene (**I**) occurs rapidly at room temperature with formation of *anti*-Markovnikov product (**II**) to be the predominate product and Markovnikov product (**III**) to be the minor (**Scheme III**).[1]

Although the addition of hydrogen halides to alkenes, one of the classical reactions of organic chemistry, is sometimes thought of as simple, there are numbers of experimental difficulties and limitations to the practical implementation of the reaction. Hydrogen chloride does not add to alkenes readily unless the alkene is either highly

Scheme I



Scheme II

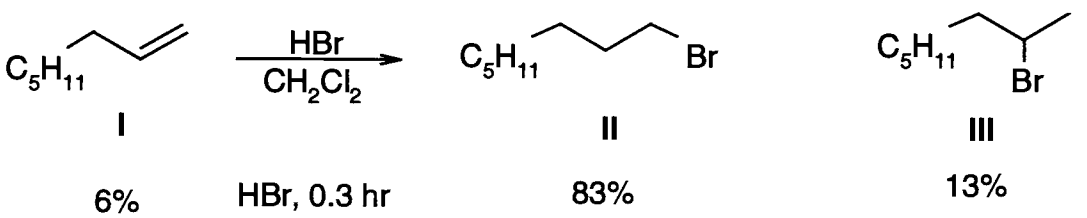


strained or substituted such that very stable carbocations may formed. Thus the hydrochlorination reaction proceeds at useful rates only when activation is enhanced by forming a stable carbocation or using a high-energy (for example, strained) reactant. Hydrogen iodide adds at useful rates, but the anhydrous form of hydrogen iodide is difficult to make and expensive. Hydrogen bromide also adds readily to most alkenes, but unless precautions are taken, addition usually involves competing of radical process to give significant amount of the anti-Markovnikov product. Moreover, producing and handling these gaseous, toxic and corrosive hydrogen halides and performing these reactions with precision is an arduous task.[1,2,3]

It has been found that silica gel or alumina facilitates ionic hydrohalogenation of alkenes, allowing the ready formation of alkyl chlorides that under uncatalyzed conditions would proceed only slowly, if at all. It has also been found that this surface-mediated addition happens selectively *syn* (under conditions of kinetic control) and the pure ionic nature of the reaction means no *anti*-Markovnikov addition of HBr occurs. Moreover, the use of various hydrogen halide precursors, such as thionyl chloride or oxalyl chloride, along with the silica gel and alumina surfaces is a convenient method for the *in situ* production of these gaseous reagents.[1,3]

Cycloheptene (**IV**), which failed to react with HCl in methylene chloride solution at either 25 °C or – 78 °C, resulted in rapid conversion to chlorocycloheptane (**V**) when silica gel was added to the reaction mixture. An even higher yield was found if thionyl chloride was used instead bubbling hydrogen chloride gas through the solution mixture (**Scheme IV**).[1]

Scheme III



I

II

III

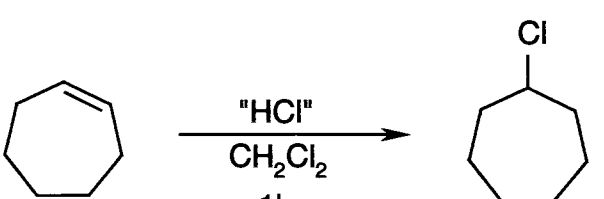
6%

HBr, 0.3 hr

83%

13%

Scheme IV



IV

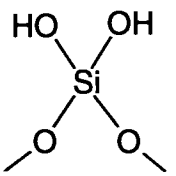
V

97%	HCl	0%
3%	HCl, SiO_2	62%
3%	$SOCl_2$, SiO_2	81%

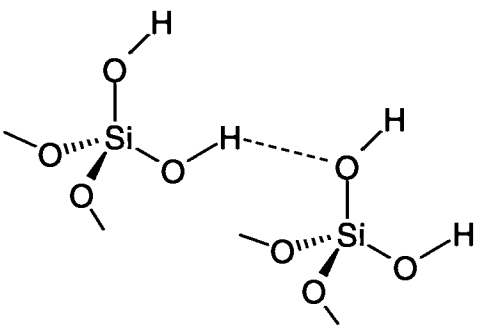
Silica gel is a polymeric compound composed of a network of silanol groups. At atmospheric pressure, silica gel absorbs moisture and thus hydrated hydroxyl groups are formed on the surface. The degree of hydroxylation is a function of temperature. The surface of hydroxylated silica gel is heterogeneous, consisting of two types of regions (**Scheme V**). One of the regions has geminal silanol groups, $Si(OH)_2$ (**VIa**), which form hydrogen bonds by interaction with adjacent geminal groups (**VIb**). The dehydroxylation of this surface is believed to form a Si-O-Si siloxane bridge (**VIc**) by the reaction of hydroxyl groups on neighboring silicon atoms. The other type of region consists of isolated silanol groups, which form in a hexagonal array of hydroxyl groups with an O-O distance of 5 Å, well beyond the limit of forming hydrogen bonding (**VII**).[4,5]

When silica gel has been equilibrated at 120 °C for 48 hours, the surfaces are totally hydroxylated with some residual physisorbed water. The geminal sites constitute about 15% of the total silanol sites.[17] Because of the hydrogen bonding, the geminal groups are more acidic (pKa 5-7) than their isolated counterparts (pKa 9.5) and are generally regarded as the active sites for promoting the hydrohalogenation reactions (**VIIIa, Scheme VI**).[4] When hydrogen chloride is added to silica gel, the HCl experiences enhancement of its acidity through hydrogen bonding interaction.[2,3] First, the HCl molecule directly bonds to the acidic proton of the hydroxyl groups on the surface (**VIIIb in Scheme VI**). Then, the polarized H-Cl bond induces protonation of cycloheptene at the surface (**VIIIc, Scheme VI**). Finally, the chloride ion that was weakly bonded to the hydroxyl group is transferred rapidly to the carbocation (**VIIId, Scheme VI**). The product here is chlorocycloheptane (**VIIIe, Scheme VI**), a

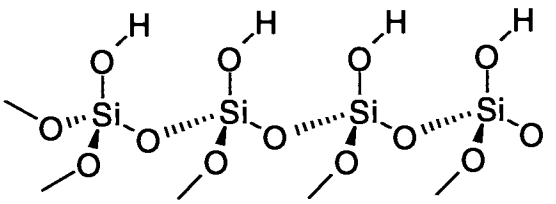
Scheme V



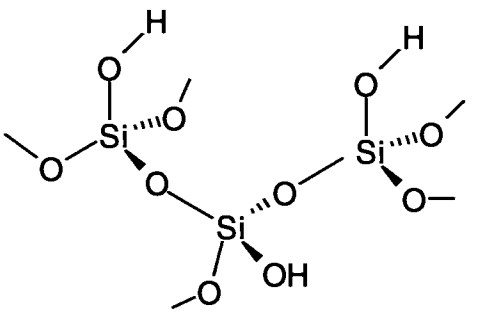
VIa



VIb

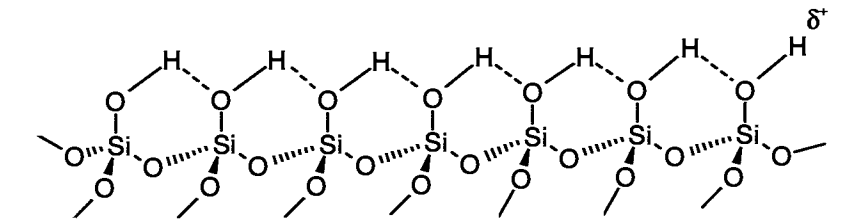


VIc

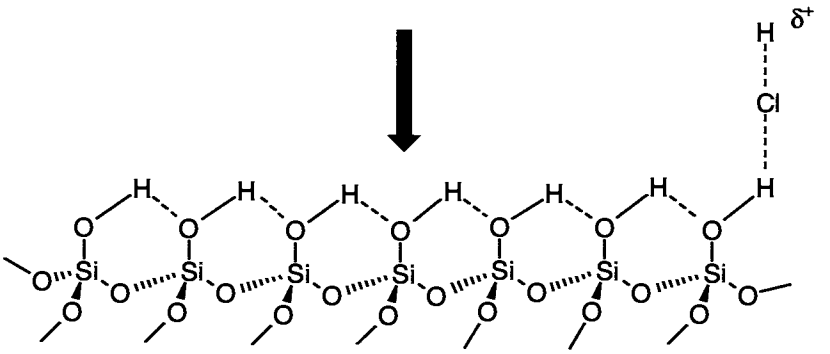


VII

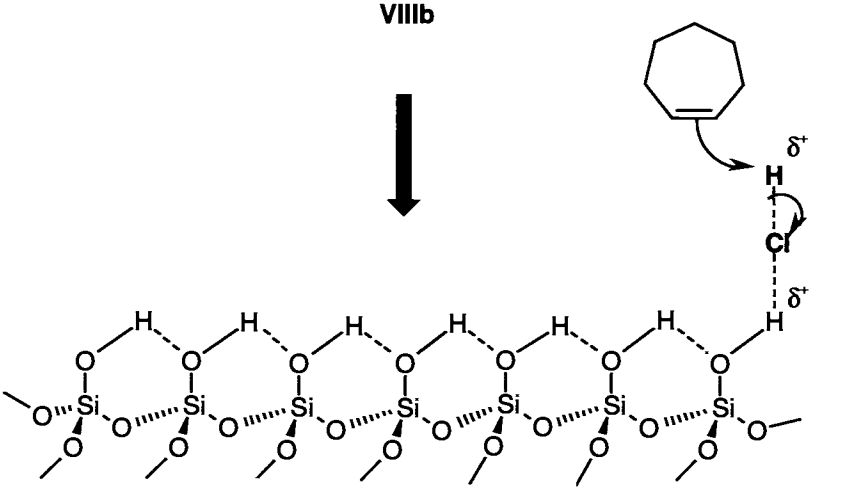
Scheme VI



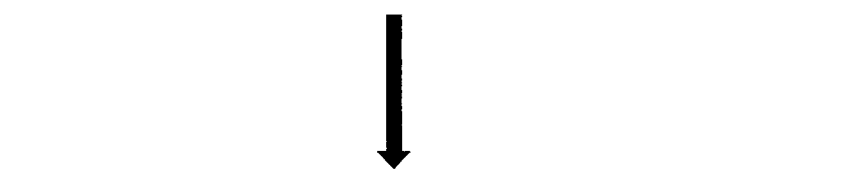
VIIIa



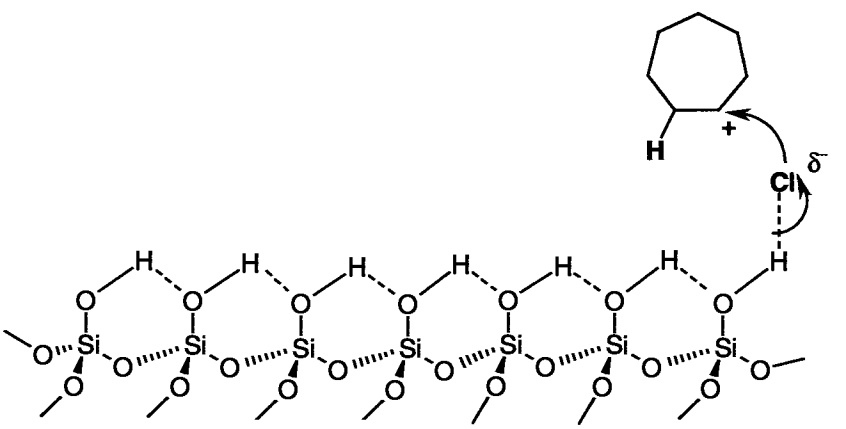
VIIIb



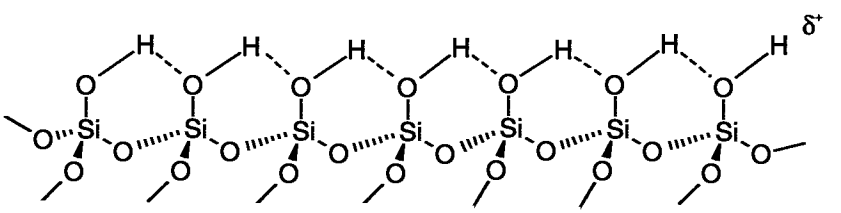
VIII



Scheme VI (continued)



VIIId



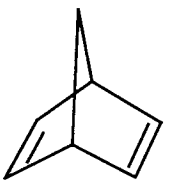
VIIIe

hydrochlorinated analog of the unsaturated starting material.

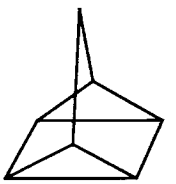
It has been found that addition of hydrogen chloride to norbornadiene (**IX**, bicyclo[2.2.1]heptadiene) or its photoisomer quadricyclene (**X**, tetracyclo[3.2.0.0.0]heptane) results in the formation of two isomers, *exo*-5-chloronorbornene (**XI**) and 3-chloronortricyclene (**XII**), as seen in **Scheme VII**.[6] Both reactions give mainly the norbornenyl adduct (**XI**). This is unusual and interesting, since most ionic additions to norbornadiene favor the homoallylic rearrangement, or nortricyclyl product.[7]

When hydrogen chloride is bubbled into a solution containing norbornadiene, it protonates one of the double bonds to form a carbocation intermediate. Two products, **XI** and **XII,** are observed by gas chromatography. When deuterium chloride is used instead of hydrogen chloride, three products are revealed by mass spectroscopic analysis. These results suggest that certain intermediates are generated allowing the positive charge be on three possible positions (**Scheme VIII**).[6,7] There are two types of rearrangements involved as shown in Scheme **IX**. First, the norbornadiene molecule **IX** is protonated to give the carbocation **XIIIa**. Next, an electron shift from the double bond gives **XIIIb** (homoallylic rearrangement). Finally, the Wagner-Meerwein rearrangement results in **XIIIc**.[7] Alternatively, a set of nonclassical cations can be proposed arguing that the intermediates **XIIIa-XIIIc** are not formed stepwise, but a single intermediate bearing a partial positive charge on three carbons (**XIV**) can be the precursor to all three products. That is, chloride ion could add nucleophilically to each of the three positions. [6,7]

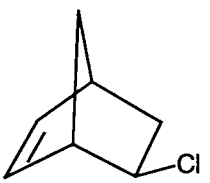
Scheme VII



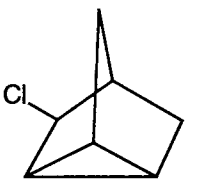
IX



X

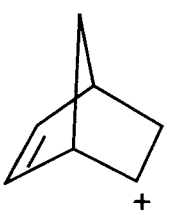


XI

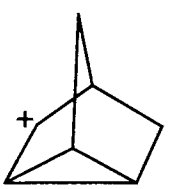


XI

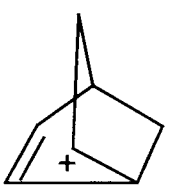
Scheme VIII



XIIIa

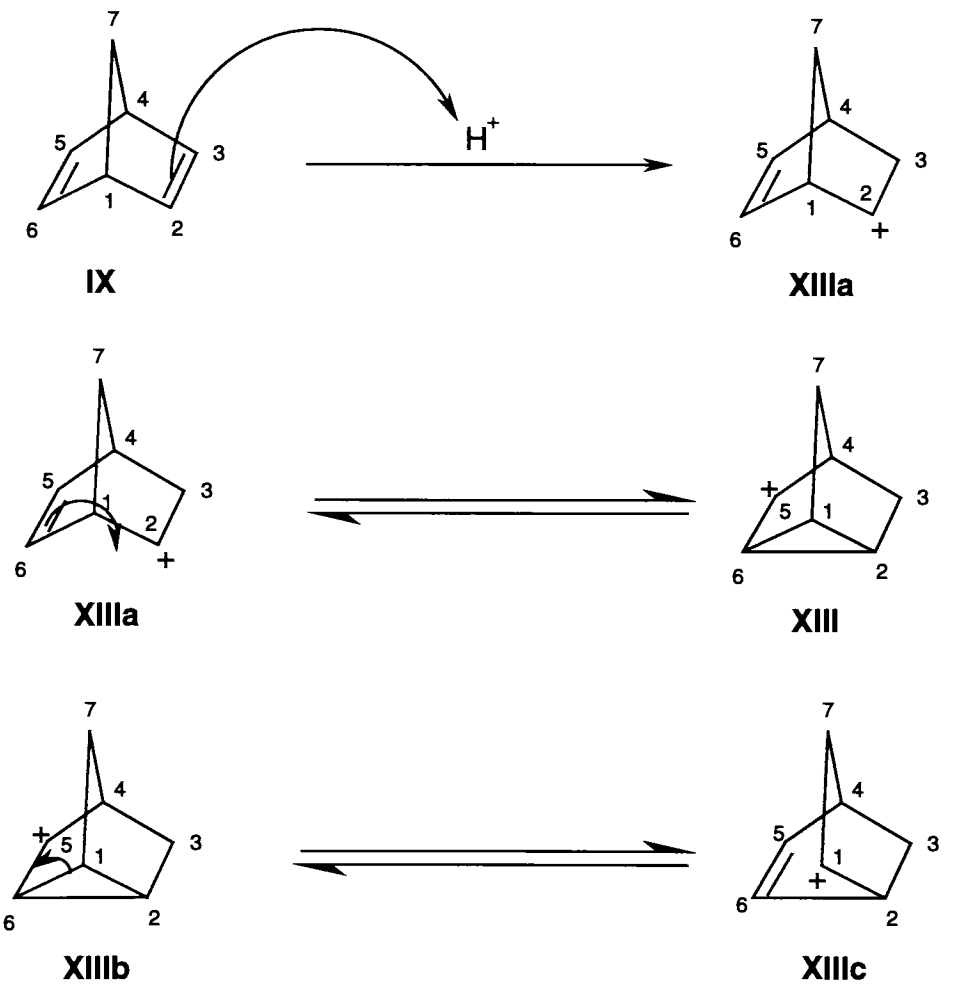


XIIIb



XIIIc

Scheme IX

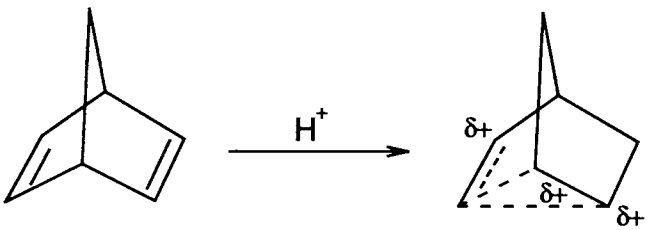


When deuterium chloride is bubbled into a solution containing norbornadiene, three isomers are produced (**XVII, XVIIa** and **XVIII, Scheme XI**), corresponding to chloride attacking each one of the three possible intermediates (**XV, XVa, XVI**).[6,8] Mass spectroscopic analysis, gives the relative amounts of norbornenyl derivatives **XVII** and **XVIIa** by taking advantage of the *retro* Diels-Alder fragmentation shown in **Scheme XII**. The peak at m/z 66, attributed to the cyclopentadiene (**XIX**) fragment, is taken as a measure of the proportion of **XVII.** The peak at m/z 67 is due to fragment **XIXa** that is taken as a measure of the proportion of **XVIIa**.[6,9]

A similar reaction takes place when hydrogen chloride is bubbled into a solution containing norbornadiene (**Scheme XIII**). As the result of chloride attacking positively charged carbons, only two products (**XI** and **XII**) are observed as per analysis by gas chromatography. The product obtained through Wagner-Meerwein rearrangement (**XIa**) is merely enantiomeric to **XI** (**Scheme XIV**), and thus can not be distinguished by gas chromatography.

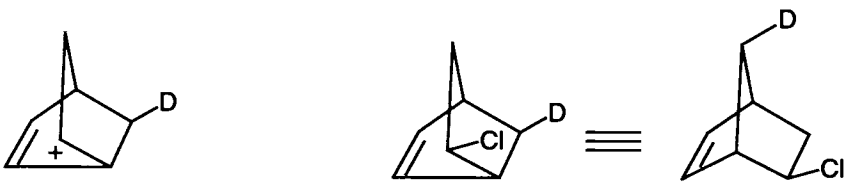
In the earlier uncatalyzed HCl addition and in our silica gel or alumina surface-mediated addition reactions, the norbornenyl adduct was always the predominate product (**Scheme XIII**). When anhydrous ferric chloride was added to the heated solution mixture containing largely norbornenyl adduct (**XI**) and a little nortricyclyl adduct (**XII**), the nortricyclyl adduct becomes the predominate product. This is assumed to be an equilibrium process and indicates that the nortricyclyl adduct is thermodynamically more stable than the norbornenyl adduct, thus suggesting that the norbornenyl adduct is the kinetically favored product.[6]

Scheme X

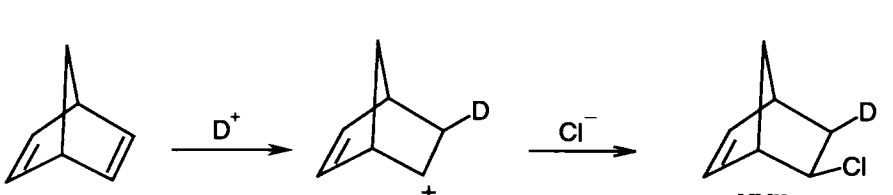


IX XIV

Scheme XI



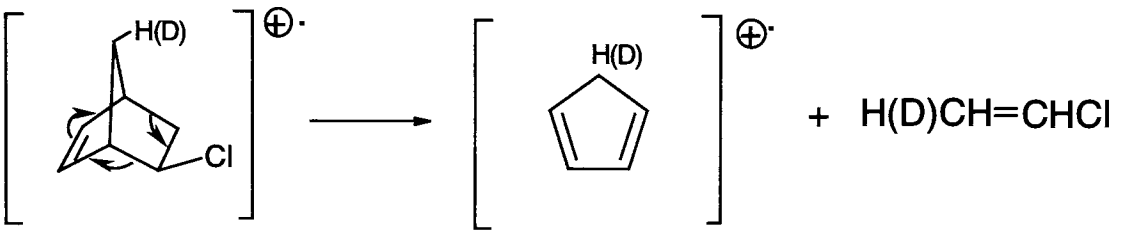
XVa XVIIa



IX XV XVII

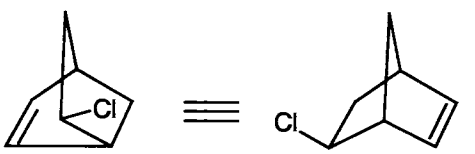
XVI XVIII

Scheme XII

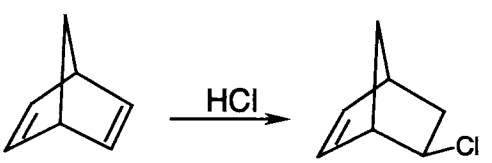


XVII(a) XIX(a)

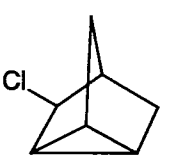
Scheme XIII



XIa



IX XI

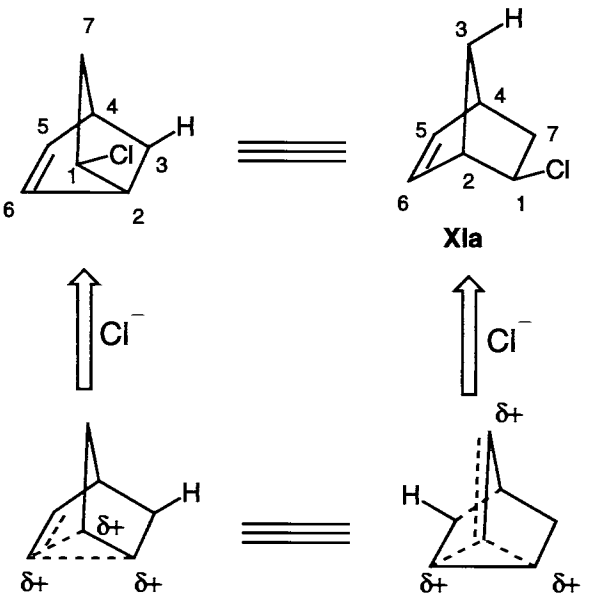


XII

It has been shown that HCl addition to alkenes is preferentially *syn* in the presence of alumina or silica gel. This is because the transfer of the chloride ion from the surface to the intermediate happens very fast and thus the chloride ion in an ion-pair intermediate has little time to migrate allowing *anti*-addition. A good example is1,2-dimethylcyclohexene (**XX**) since when it is treated with oxalyl chloride in the presence of alumina , it undergoes rapid addition (**Scheme XV**), and initially gives *cis*-1-chloro-1,2-dimethylcyclohexane (**XXIa**) as the predominate product and *trans*-1-chloro-1,2-dimethylcyclohexane (**XXIb**) as the minor product.[1]

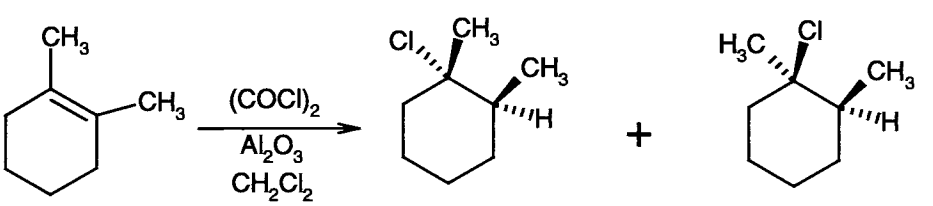
It was our desire to study the hydrohalogenation of norbornadiene (**IX**) and quadricyclene (**X**) under various experimental conditions mediated by alumina and silica gel surfaces to gain understanding for the mechanism of this process and therefore develop useful methods of achieving isomer control. Isomer control would mean formation of a greater proportion of **XI** vs. **XII**, and of **XVII** vs. **XVIIa** and **XVIII**.

Scheme XIV



XIa

Scheme XV

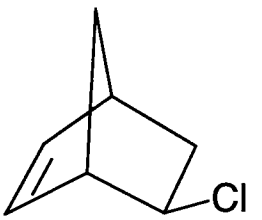


XX XXIa XXIb

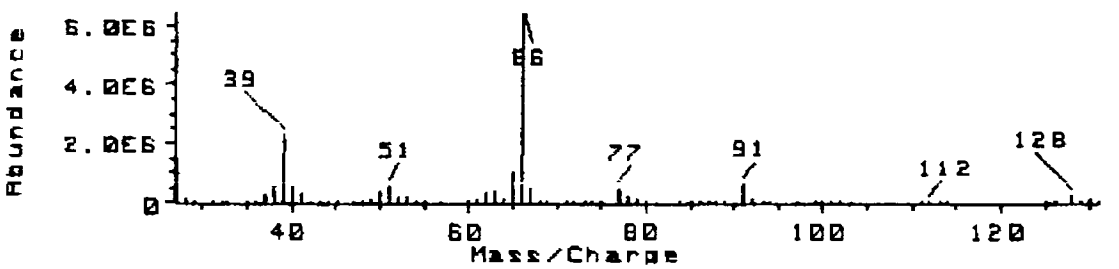
RESULTS AND DISCUSSION

When pretreated at 120 °C at atmospheric pressure for at least 48 hours, the surface of silica gel or alumina was found to promote hydrochlorination of norbornadiene and quadricyclene in a solution containing either thionyl chloride or oxalyl chloride as the chlorinating agent (**Scheme XVI**). This resulted in the formation of two isomers, *exo*-5-chloronorbornene (**XI**) and 3-chloronotricyclene (**XII**). The mass spectra of these products are shown in **Figure I** and **Figure II**. Identifying characteristics of **XI** and **XII** including mass spectra have been published previously.[6] Variations in experimental parameters like catalyst, reaction time, solvent, and reaction temperature cause changes in product ratios and yields. This information provides insight into the details of the reaction mechanism.

Hydrochlorination was carried out by adding thionyl chloride to a reaction vessel contain norbornadiene, pretreated silica gel, and methylene chloride solvent. After one hour at room temperature, a mixture of 70% (± 1%) *exo*-5-chloronorbornene and 30% 3-chloronotricyclene were obtained in 29% total yield. The norbornadiene was not entirely consumed until the reaction time was extended beyond twelve hours (**Table 2**). When the one-hour reaction was carried out using alumina instead of silica gel, all of the norbornadiene was consumed, and it gave rise to approximately the same product ratio of **XI** and **XII** and a higher yield of 42% was obtained (**Table 1**). It is known that a fully hydroxylated surface of silica gel has an average of 4.6 OH/100 $Å^2$, whereas a fully hydroxylated alumina has 12.5 OH/100 $Å^2$.[10] So, with the same amount used, the active

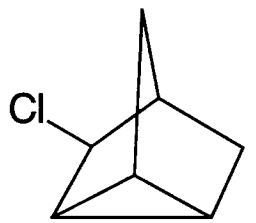


XI

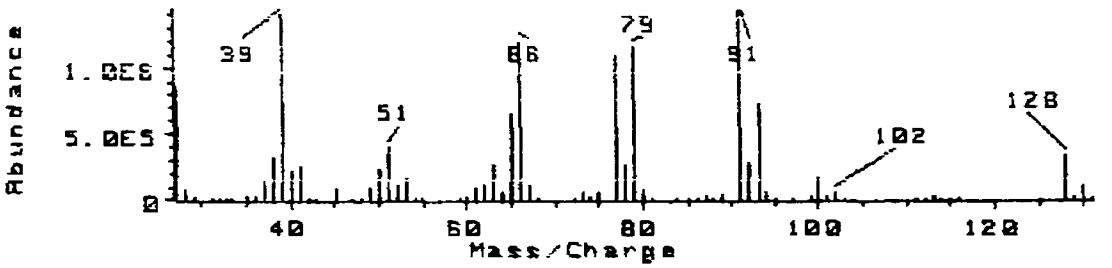


m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
27.10	1461760	47.95	24080	68.95	1621	93.15	70944
28.10	100920	49.05	124000	71.05	1367	94.15	7013
29.10	13412	50.05	386816	71.95	5597	97.00	2548
31.10	9225	51.05	585408	73.05	51376	99.00	12426
32.10	4525	52.05	178752	74.05	34288	100.00	9637
32.75	1930	53.05	163904	75.05	56488	101.00	5628
34.95	45104	54.05	16321	77.05	494976	102.00	3197
35.95	46216	55.05	2120	78.05	196544	103.10	1117
37.05	244096	56.95	975	79.05	120032	111.00	2263
38.05	550080	59.95	22560	80.05	8853	111.90	6180
39.05	2297856	61.05	126376	83.95	5326	113.00	5801
40.05	563648	62.05	318272	85.05	11262	114.00	2334
41.05	308096	63.05	400704	86.05	17752	125.00	3361
42.05	12839	64.05	135552	87.05	11293	126.10	1500
43.05	19160	65.05	1033856	88.05	8066	128.00	229312
44.05	13087	66.05	6447616	89.05	46976	129.00	17848
45.05	56184	67.05	457536	91.05	636736	130.00	77376
46.95	13339	68.05	13376	92.05	78432	131.00	5082

Figure I : The mass spectrum of *exo*-5-chloronorbornene



XII



m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
27.10	855360	49.05	88608	73.05	53072	95.15	2899
28.10	76960	50.05	223232	74.05	25224	97.00	3179
29.10	17280	51.05	396352	75.05	57888	99.00	20176
31.10	7368	52.05	112472	77.05	1102848	100.00	157760
32.00	3604	53.05	168832	78.05	256960	101.00	17952
32.75	1313	54.05	15582	79.05	1161216	102.00	52360
33.25	1566	54.95	3315	80.05	75512	103.00	3810
34.95	21952	59.15	1517	81.05	2795	111.00	3564
35.95	30016	60.05	16768	83.95	3594	112.00	11606
37.05	148672	61.05	85536	85.05	9690	113.00	46088
38.05	317440	62.05	130552	86.05	14675	114.00	6283
39.05	1399808	63.05	264768	87.05	17848	115.00	14398
40.05	211456	64.05	63824	88.05	14556	116.00	1571
41.05	252160	65.05	654208	89.05	43896	125.00	5817
42.05	10041	66.05	1206272	91.05	1454080	128.00	334208
42.95	15040	67.05	109168	92.05	282496	129.00	26344
45.05	90552	68.05	7129	93.15	745024	130.00	105392
46.95	10840	72.05	4639	94.15	54536	131.00	8520
47.95	14958						

Figure II : The mass spectrum of 3-chloronortricyclene

Table 1: Hydrochlorination Using Alumina Catalyst

Mole ratio of Norbornadiene/ $SOCl_2$	Solvent	Time (hrs)	XI %	XII %	Yield (XI + XII) %
1:2	CH_2Cl_2	1	70.7	29.3	*
1:2 [(a)]	CH_2Cl_2	1	73.0	27.0	33.0
1:2	CH_2Cl_2	1	71.1	28.9	41.7
1:2	CH_2Cl_2	6	68.7	31.3	41.9
1:2	1,4-Dioxane	2	63.3	36.8	**

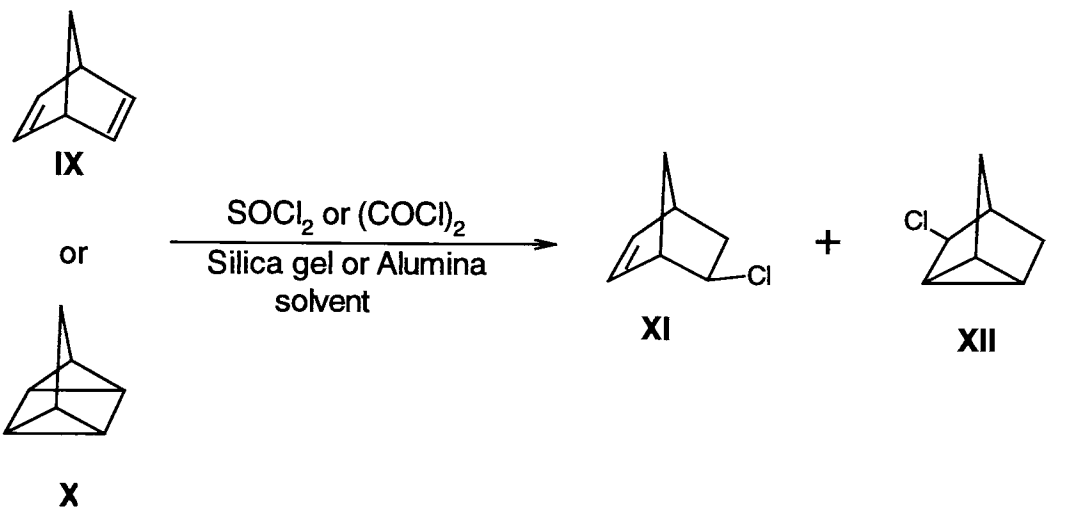
* spilled during purification step prevented yield calculation based upon solution concentrations.
** evaporation losses (reaction solvent) prevented yield calculation based upon solution concentrations.
(a): quadricyclene was used instead of norbornadiene.

Table 2: Hydrochlorination Using Silica Gel Catalyst

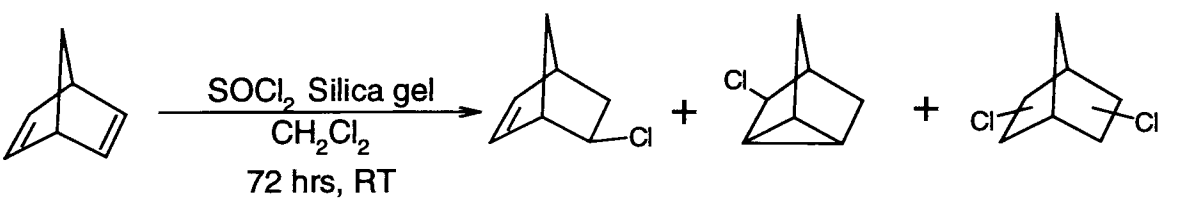
Mole ratio of Norbornadiene/ SOCl2	Time (hrs)	XI %	XII %	Yield (XI + XII) %	Net Yield (XI + XII) %
1:2	1	69.9	30.1	28.8	34.7
1:2	2	71.0	29.0	*	*
1:1	1	70.2	29.8	18.6	25.6
1:1.5	1	69.0	31.0	17.9	21.9
1:2	2	70.1	29.9	37.9 [(b)]	39.0
1:2	6	68.0	32.0	55.8 [(b)]	55.8
1:2	1	69.2	30.8	25.3 [(c)]	33.0
1:2	10 min	67.1	32.9	1.5 [(c)]	2.2
1:2	12	69.2	30.8	53.0	53.0
1:2	72	60.2 [(d)]	34.2	*	*
1:2	1	73.5	26.5	1.2 [(e)]	1.6
1:2	6	46.6	53.4	6.3 [(e)]	9.1
1:2	72	44.4	55.6	25.4 [(e)]	28.1
1:2	1	ND	ND	- [(f)]	-
1:2	1	79.4	20.6	19.6 [(g)]	20.1

(b) 60g of silica gel was used instead of standard 30g
(c) $(COCl)_2$ was used replacing $SOCl_2$ as the chlorinating agent
(d) 5.6% diadduct was formed (gas chromatography)
(e) Anhydrous ethyl ether was used replacing methylene chloride as the reaction solvent
(f) 1,4-dioxane was used replacing methylene chloride as the reaction solvent
(g) Hexane was used replacing methylene chloride as the reaction solvent

Scheme XVI



Scheme XVII



site that responsible for promoting the hydrochlorination on the surface of silica gel is much less than alumina. Under the same experimental conditions, alumina yielded more products than silica gel.

When 60g of silica gel (instead of 30g) was used for at two hours, not surprisingly, almost all of the norbornadiene was consumed and a 39% yield was obtained. When the run time was extended to six hours with 60g silica gel, virtually all of the norbornadiene was consumed and a 56% yield was detected by gas chromatography (**Table 2**). Comparing the results of all the experiments carried out with silica gel at room temperature in methylene chloride suggested that the amount of silica gel used and the reaction run time played important rolls on the product yield, but had little to do with the **XI** to **XII** product ratio.

When the reaction time was extended to 72 hours using silica gel as the catalyst at room temperature (**Table 2**), the proportion of 3-chloronotricyclene was slightly increased from 30% (± 1%) to 34% and the proportion of *exo*-5-chloronorbornene had decreased from 70% to 60%, with formation of 6% dichloro adduct (**Scheme XVII**). Another member of our lab, William P. Gallagher (whose research projects mainly focus on dichloro adducts) found that the formation of dichloro adducts was favored by use of alumina rather than silica gel. Under alumina catalyzed hydrochlorination conditions, after six hours in hexane, the formation of the diadducts could reach over 90% in total (**Table 4**).[11] If we assume that the formation of dichloro adducts came only from protonation of the remaining double bond in *exo*-5-chloronorbornene (**XI**), the dichlorinated products then can be considered as a derivative of **XI** only, and thus by

Table 3: Hydrochlorination Using Deuterated Alumina Catalyst

Temp.	(XI + XVII + XVIIa) %	(XVIII + XII) %	XVIIa / XVII % / %	Deuteration %
25 °C	69.2	30.8	32.3 / 67.7	63.3
0 °C	70.4	29.6	35.0 / 65.0	65.3
-78 °C	73.0	27.0	36.3 / 63.7	26.4
25 °C [(c)]	66.3	33.7	37.8 / 62.2	20.9

Table 4: Formation of Diadducts (W. P. Gallagher)[11]

Alumina (g)	Solvent	Time (hrs)	XI	XII	Diadduct
30	1,4-dioxane	1	68%	32%	ND
30	Hexane	3	51%	23%	26%
60	Hexane	1	44%	20%	36%
60	Hexane	1	47%	19%	34%
60	Hexane	6	1%	3%	96%
60	Hexane	6	-[i]	-[i]	92%
60[h]	Hexane	1	78%	22%	ND
30[h]	1,4-dioxane	4	17%	83%	ND

(h): silica gel was used instead of alumina
(i): data not available

Table 5: Inter-conversion Between Norbornadiene and Quadricyclene during the Reaction of Quadricyclene with Oxalyl Chloride and Alumina (R. Bader)[14]

Time	Temp. (°C)	% quadricyclene	% norbornadiene
2 min.	26	88	12
60 min.	26	23	77
120 min.	26	36	64
240 min.	26	17	83

combining the proportions of *exo*-5-chloronorbornene and diadducts, we have an idea as to products associated with **XI**. Results obtained in such fashion again show that the norbornenyl adduct is the predominate product for catalyzed hydrochlorination in methylene chloride or hexane solvent. For example, when the reaction was promoted by 60g alumina using hexane solvent at room temperature, after one hour, 44% *exo*-5-chloronorbornene and 36% diadduct were obtained, (**Table 4**), and thus based on our assumptions, a total of 80% norbornenyl adduct was formed at one time in this reaction.

With both silica gel and alumina, there appeared to be a solvent effect, with the more polar solvent favoring the homoallylic rearrangement product leading to 3-chloronotricyclene. For example, when the reaction was promoted by alumina using 1,4-dioxane solvent, 37% 3-chloronotricyclene was obtained, whereas methylene chloride, a less polar solvent, gave only 29% (**Table 1**). In the case of silica gel, the proportion of *exo*-5-chloronorbornene increased to 80% when hexane was used (**Table 2**). With ethyl ether, a more polar solvent, after six hours, the thermodynamically favored product 3-chloronotricyclene became slightly predominant (**Table 2**). All these results suggest that the carbocation has a longer life in the more polar solvent giving it a chance to rearrange to the precursor to 3-chloronotricyclene.[7] After the norbornadiene is protonated by a process on the surface of the silica gel or alumina, the initially formed intermediate (**XIIIa**), which gives the norbornenyl adduct, is trapped quickly in the less polar solvent, minimizing rearrangement. In the case of the dichloro compounds, William P Gallagher's data revealed that diadduct formation was favored in the less polar hexane solvent (**Table 4**). This suggests that HCl, or its equivalents are less reactive in polar solvent. Another possibility is that the more polar solvent deactivates the norbornenyl

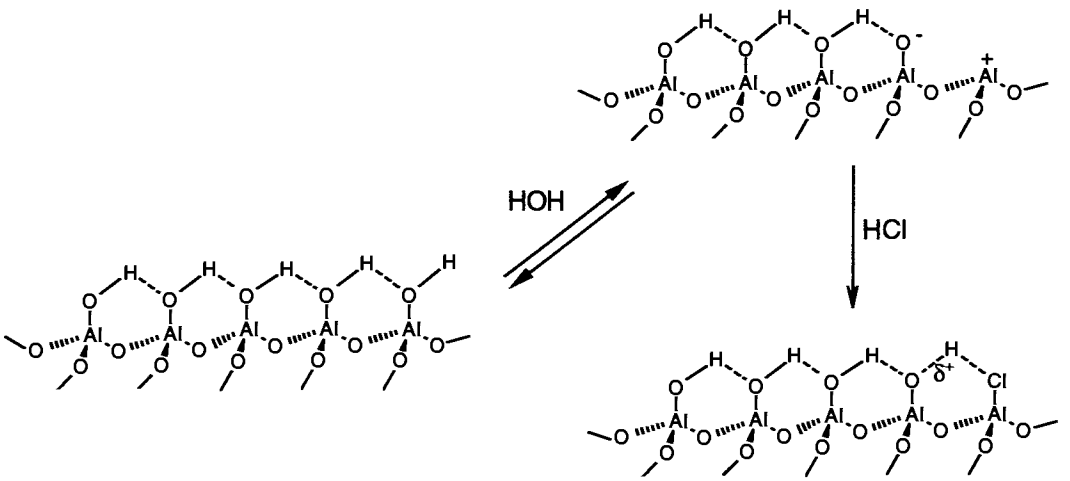
adduct, hence preventing a second HCl addition. In other words, the carbocation necessary to from the diadduct forms less readily in the non-polar solvent.

Ethyl ether has lone-pair electrons that can serve as hydrogen bond acceptors, and thus ether can bond to the hydroxyl group on the surface of silica gel. When thionyl chloride is added to a stirred suspension of silica gel in ethyl ether, the active sites of silica gel may have been already well blocked by ethyl ether through hydrogen bonding. Hence, the HCl molecule has to compete with ethyl ether over the activate sites on the surface, which results in slow addition. After one hour of reaction time, only about a 1% yield of product was detected. When the reaction time was increased to 72 hours, the yields increased to 25%, but still left unreacted norbornadiene (**Table 2**).

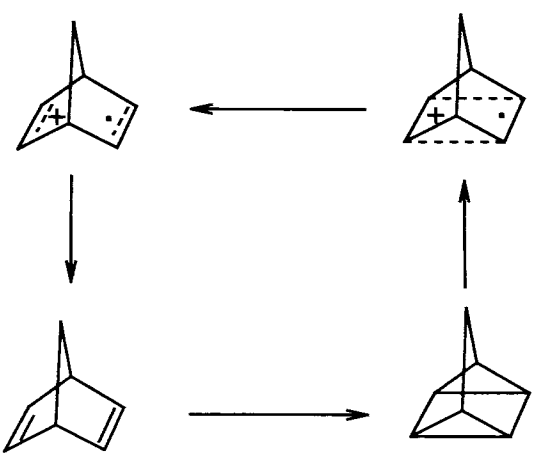
It has been reported that for hydrochlorination reaction, oxalyl chloride combined with alumina provided the best results.[3] Using silica gel, both thionyl chloride and oxalyl chloride seemed to work fine, although not as good as with alumina. A "standard" ratio of 70% *exo*-5-chloronorbornene vs. 30% 3-chloronotricyclene was observed (**Table 2**). The molar ratio between the two reagents, norbornadiene and thionyl chloride, has also been studied using silica gel catalysis (**Table 2**). The relative proportions of the products for all three experiments stayed constant, whereas using a 1:2 molar ratio (norbornadiene : thionyl chloride) gave a higher yield than when 1:1.5 and 1:1 molar ratios were used.

Norbornadiene and quadricyclene are photoisomers, and the conversion of quadricyclene to norbornadiene can be achieved readily (**Scheme XVIII**).[12] Quadricyclene also undergoes hydrochlorination when thionyl chloride was added to pretreated alumina and methylene chloride solvent (**Scheme XVI**), affording 73% *exo*-5-

Scheme XIX



Scheme XVIII



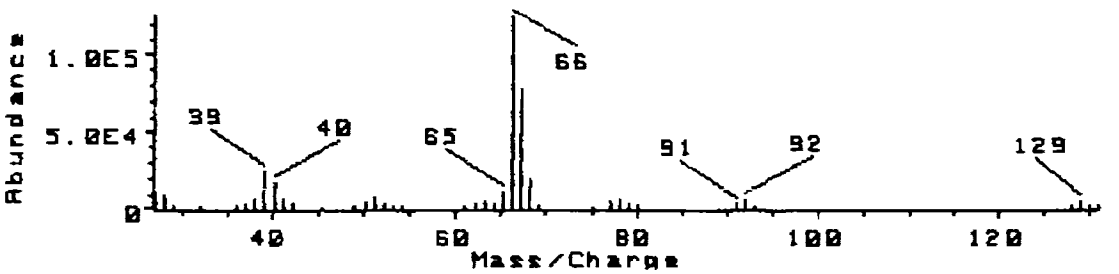
chloronorbornene and 23% 3-chloronotricyclene with 33% yield after one hour at room temperature (**Table 1**). A graduate student in our laboratory, T. Greenwood, found that when hydrochlorination was carried out by alumina in ethyl ether solvent under room temperature, after one hour neither quadricyclene nor norbornadiene were totally consumed. Analysis revealed that 98% norbornadiene remained as starting material in both reactions.[13] R. Bader, another undergraduate research student working in our laboratory, carried out other studies. By tracking the percentage of unreacted quadricyclene versus percentage of unreacted norbornadiene during the reaction of quadricyclene with oxalyl chloride and alumina at room temperature, she obtained increasing amounts of unreacted norbornadiene with increasing reaction time (**Table 5**).[14] This suggests that hydrochlorination of quadricyclene is accompanied by conversion of quadricyclene to norbornadiene, and the product formed in this reaction has formed to a significant degree by hydrohalogenation of norbornadiene.

The surface of γ-alumina is heterogeneous, similar to the surface of silica gel, but basic. As a result of equilibration with atmospheric moisture at 120 °C for at least 48 hours the surfaces of alumina are terminated by a monolayer of hydroxyl groups.[15,16] This monolayer, however, is not the site of hydrochlorination. There are some sites consisting of an oxide ion and adjacent exposed aluminum cation that formed by removal of chemisorbed water on at 120 °C. Neutralizing these sites, the hydrogen chloride provides the active sites that promote the reaction (**Scheme XIX**).[2] Besides catalyzing the addition reaction, the surfaces also hydrolyze the hydrogen chloride precursors. The formation of HCl involves the reaction of the chlorinating precursors with residual water physisorbed to the surface and / or with hydroxyl groups on the surface itself. When

alumina being replaced by deuterated alumina, which containing mostly a monolayer of deuterium oxide, hydrolysis of the precursors would results in the formation of deuterium chloride. This could then lead to the addition of DCl to norbornadiene.

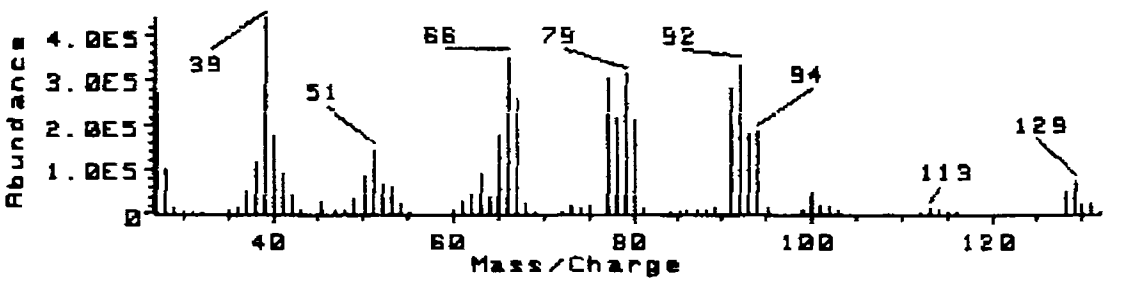
Deuterated alumina (commercially available from Aldrich) and thionyl chloride in methylene chloride solution were found to result in the addition of DCl to norbornadiene (**Scheme XX**). Three deuterated products: *exo,exo*-6-chloro-bicyclo[2.2.1]hept-2-ene-5-d (**XVII**), *exo,anti*-5-chlorobicyclo[2.2.1]hept-2-ene-7-d (**XVIIa**) and 5-chlorotricyclo[2.2.1.$0^{2,6}$]heptane-3-d (**XVIII**), as well as the two undeuterated products of *exo*-5-chloronorbornene (**XI**) and 3-chloronotricyclene (**XII**) were detected by GC/MS (**Scheme XXI**). The mass spectra of the deuterated product are shown in **Figure III** and **Figure IV**.

If we compare the earlier results obtained from the non-catalyzed DCl addition, which gave a ratio of 43%/57% for **XVIIa/XVII**, to the surface catalyzed addition, which gives a ratio of 32.3%/67.7% (**Table 3**), it is clear that there is less Wagner-Meerwein rearrangement in the catalyzed addition. The fact that catalyzed reaction disfavors the rearranged adduct (**XVIIa**) may be due to the rapid trapping of the cation by chloride ion. Once the norbornadiene is protonated, the chloride ion traps the intermediate before it has time to rearrange. As the reaction temperature is decreased, we find that the ratio of the Wagner-Meerwein rearrangement product (**XVIIa**) increases slightly from 32% to 36% and the 1,2-addition product (**XVII**) decreases from 68% to 64% (**Table 3**). Since the overall proportion of the norbornenyl adduct has slightly increased as the reaction temperature decreases, we again conclude that the norbornenyl adduct is the kinetic product.



m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
27.10	11262	42.10	3296	63.10	5737	79.05	3251
28.10	9851	45.50	1286	64.10	3006	80.05	1617
29.10	1513	49.00	1688	65.10	10693	91.05	3390
32.00	1589	50.10	4875	66.10	125696	92.05	6693
36.00	2219	51.10	7511	67.10	78216	93.05	2665
37.00	3057	52.10	4257	68.10	20288	128.05	1466
38.10	7228	53.10	2725	69.10	1491	129.05	4875
39.10	23496	54.10	2151	75.10	1127	130.05	2269
40.10	17000	61.00	1603	77.10	5166	131.00	1580
41.10	6265	62.10	3100	78.10	5946		

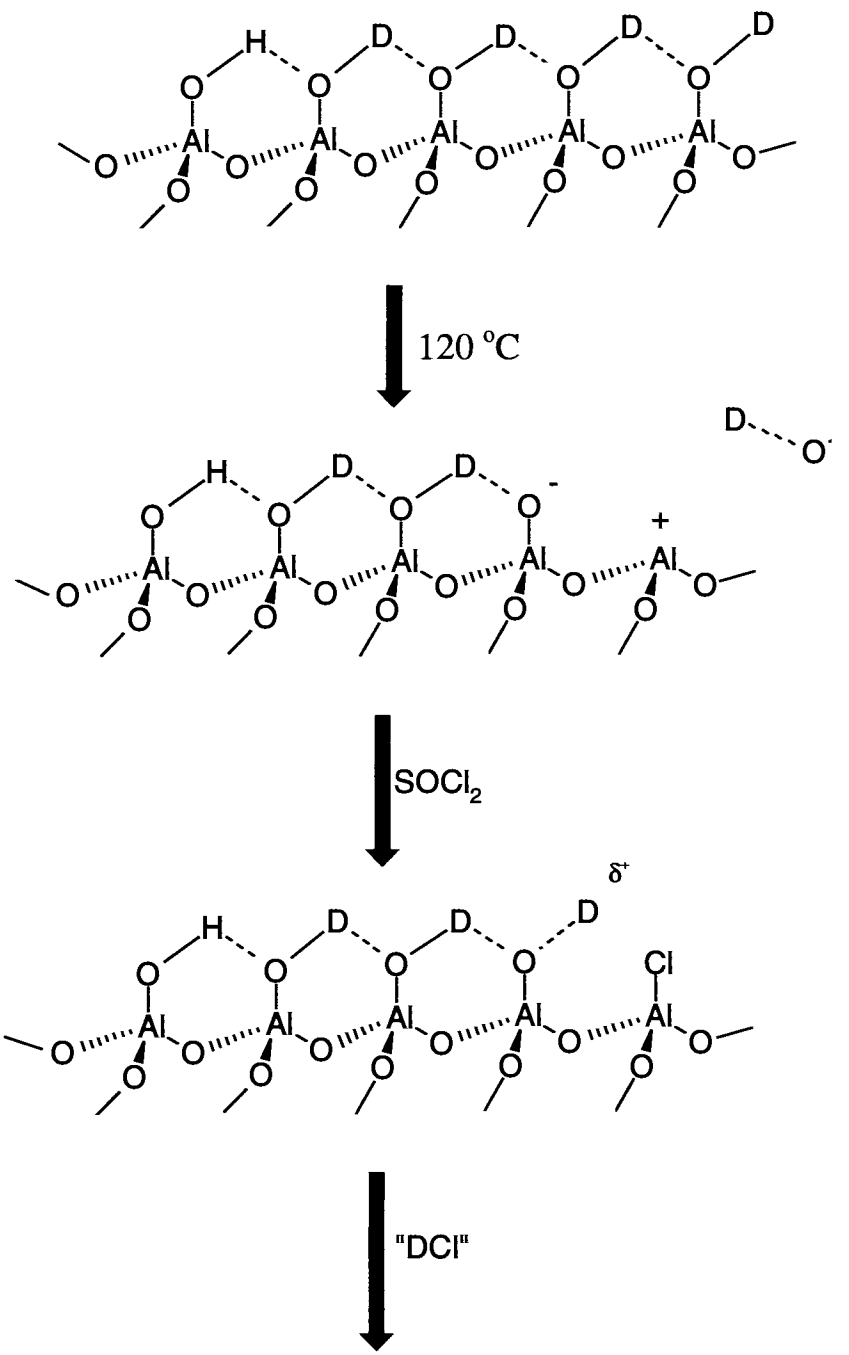
Figure III : The mass spectra of 39% *exo*-5-chloronorbornene
41% *exo,exo*-6-chlorobicyclo[2.2.1]hept-2-ene-5-d and
20% *exo,anti*-5-chlorobicyclo[2.2.1]hept-2-ene-7-d



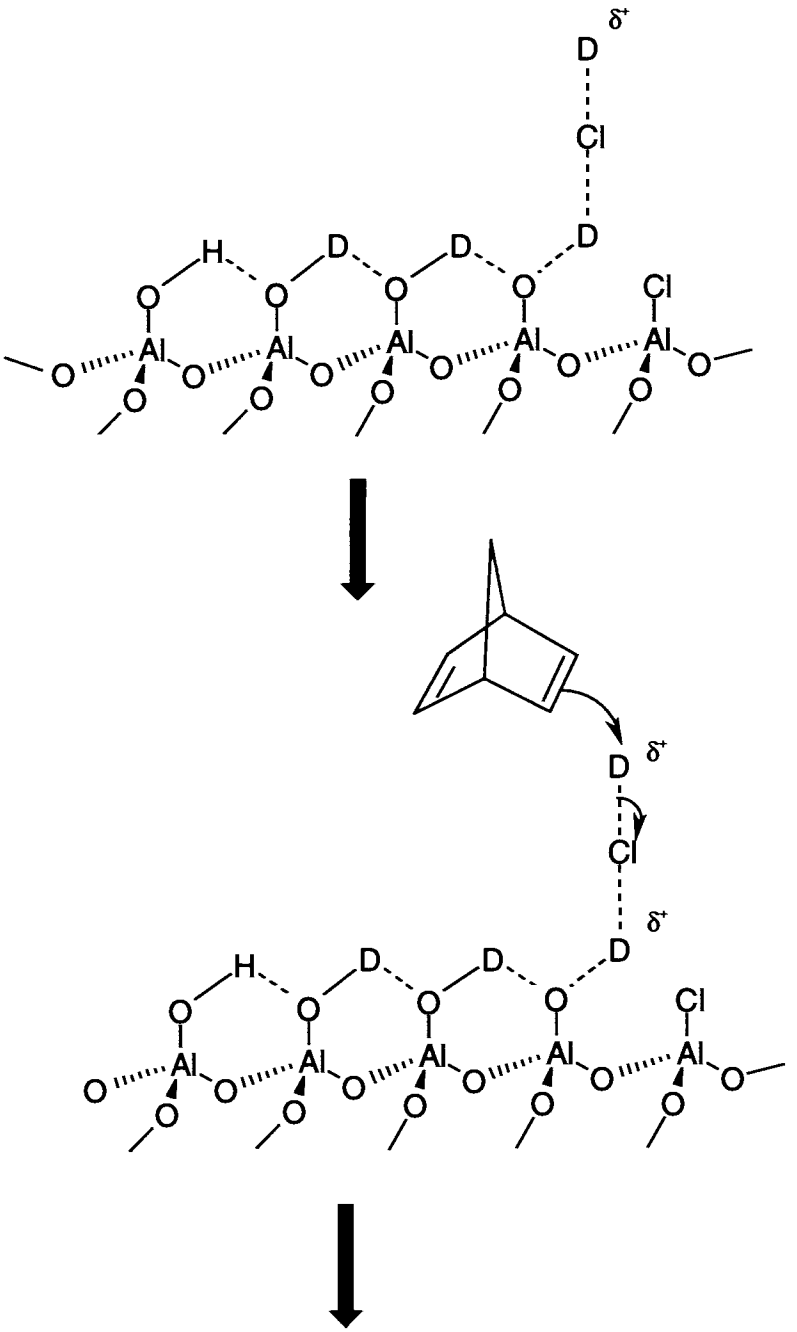
m/z	abund.	m/z	abund.	m/z	abund.		abund.
27.10	269824	49.00	32208	73.00	18752	94.05	185664
28.10	98488	50.10	81912	74.10	10124	95.15	13934
29.10	10869	51.10	142720	75.10	19960	99.05	7129
30.10	2635	52.10	64168	77.10	307264	100.05	48264
31.00	2748	53.10	56184	78.10	219008	101.05	18496
32.00	1407	54.10	24880	79.05	313152	102.05	16816
35.00	8544	55.10	3747	80.05	211456	103.05	5535
36.00	11262	60.00	6335	81.05	14319	112.05	2907
37.00	50272	61.10	28344	84.05	1571	113.05	11798
38.10	113392	62.10	41688	85.05	3215	114.05	7032
39.10	438144	63.10	87648	85.95	5535	115.05	4187
40.10	178752	64.10	40680	87.05	5597	116.05	2026
41.10	89088	65.10	176320	88.05	5326	128.05	47232
42.10	42952	66.10	352768	89.05	11386	129.05	75104
43.10	6785	67.10	256256	91.05	285632	130.05	20568
45.50	27584	68.10	23688	92.05	337856	131.00	24408
46.80	5311	69.10	1958	93.05	183168	132.00	1752
48.00	5311	72.10	1909				

Figure IV : The mass spectra of 63% 5-chlorotricyclo[2.2.1.$0^{2,6}$]heptane-3-d and 37% 3-chloronotricyclene

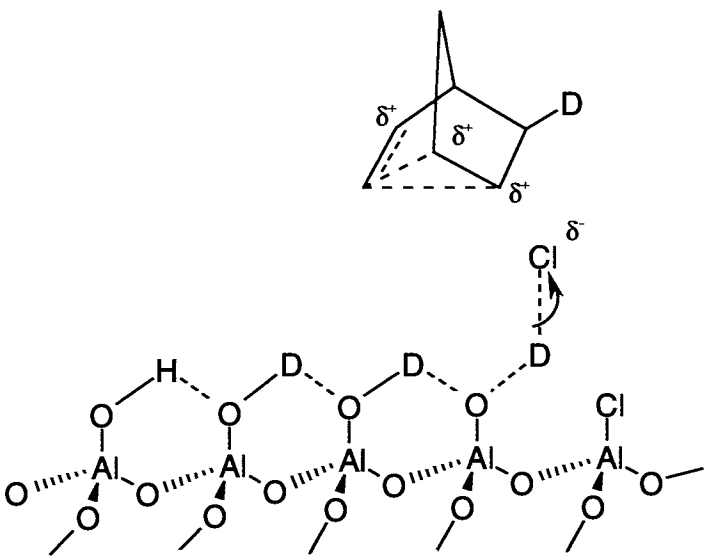
Scheme XX

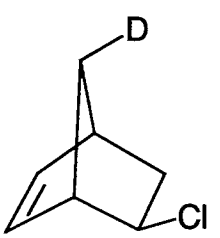


Scheme XX (continued)

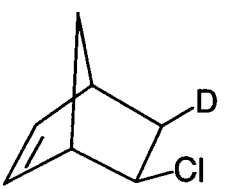


Scheme XX (continued)

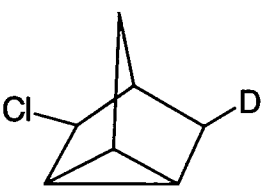




XVIIa

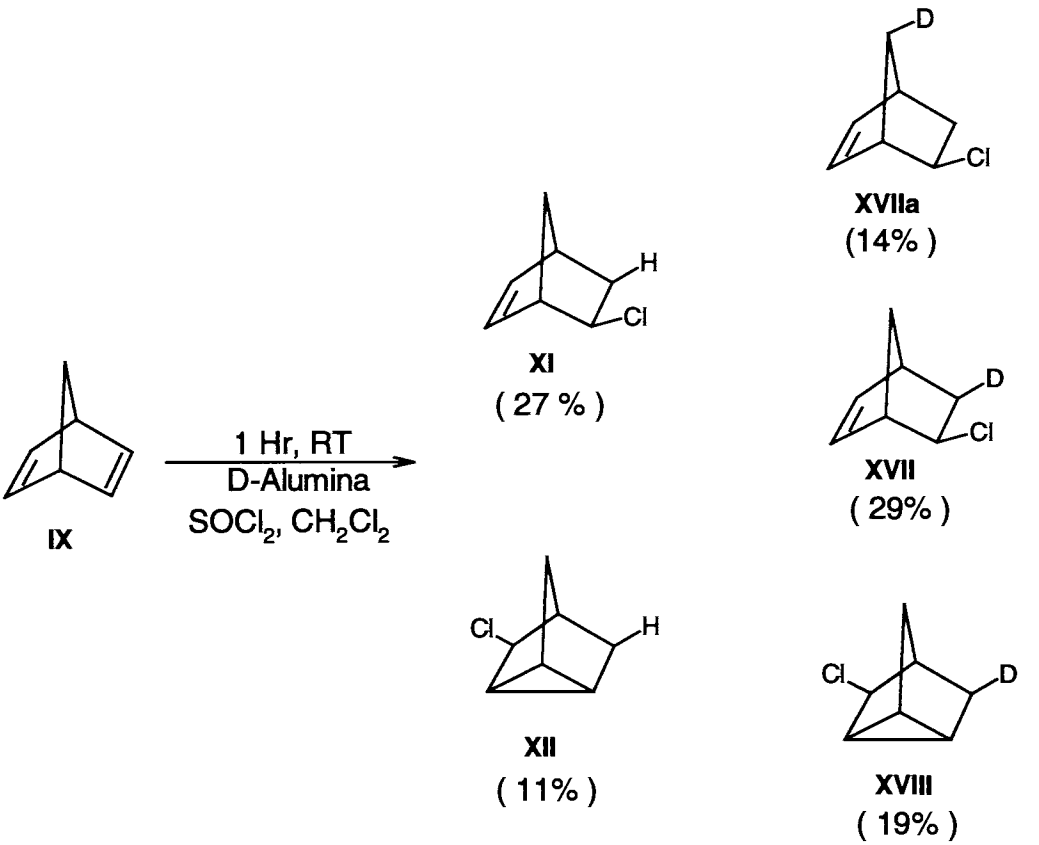


XVII



XVIII

Scheme XXI


IX
1 Hr, RT
D-Alumina
SOCl2, CH2Cl2
XI
(27 %)
XII
(11%)
XVIIa
(14%)
XVII
(29%)
XVIII
(19%)

When oxalyl chloride was used in the catalyzed DCl addition of norbornadiene, both the proportions of Wagner-Meerwein rearrangement product and of homoallylic rearrangement products increased slightly compare to the results obtained with thionyl chloride. Since oxalyl chloride is a weaker chlorinating agent than thionyl chloride, the addition apparently is slow enough to allow equilibration of the intermediate, leading to larger amounts of rearranged products.

EXPERIMENTAL

Standard Preparative-Scale Hydrochlorination Reaction. A sample of 30 g of 230-400 mesh Merck grade 9385 silica gel (Aldrich cat. no. 22,719-6), which had been equilibrated at 120 °C for at least 48 hours, was placed into a 500 ml three neck round-bottomed flask under N_2. After the contents of the flask had cooled, 250 ml of methylene chloride (J. T. Baker, cat. no. 9324-01) and 0.05 mole (~4.6 g) of bicyclo[2.2.1]hepta-diene (norbornadiene, Aldrich, cat. no. B3,380-3) were added and the mixture was stirred with a magnetic stirrer at room temperature. The reaction was initiated when 0.10 mole (~11.9 g) of thionyl chloride (Aldrich, cat. no. 23,046-4) was added to the flask.

After one hour, the methylene chloride solution was decanted from the silica gel to stop the reaction. The remaining silica gel in the flask was washed with an additional 75 ml of methylene chloride and the washes were combined with the mother liquor. The methylene chloride solution was then filtered through Whatman (cat. no. 1001 125) filter paper to remove any residual silica gel. The residual thionyl chloride in methylene chloride solution was removed by washing four times with 500 ml of 1M aqueous sodium carbonate solution. The solution was then gravity filtered after drying with anhydrous sodium sulfate. BHT (butylated hydroxyl toluene) was added (1% wt/wt) to keep the product from polymerizing. After the methylene chloride was removed by rotary evaporation, the mixture was analyzed by gas chromatography.

Purification was done by flash chromatography using methylene chloride and silica gel. The fraction of the eluent containing the products was collected. After the

solvent was removed by rotary evaporation, the mixture was distilled. A mixture of 70% *exo*-5-chloronorbornene and 30% 3-chloronortricyclene was obtained.

Analyzing Samples by Gas Chromatography. A Hewlett Packard 5890 capillary gas chromatography with FID detector and HP-5 column (30 m x 0.25 mm, 0.25 μm film thickness, part no. 19091J-433) was used. The split flow rate was 1.0 ml/min. Both the injector and the detector temperature were set at 250 °C. The oven was initially 100 °C, and then it was increased to 250 °C at 10 °C/min., and finally stay at 250 °C for15 min, in order to clean the BHT in the column. The injection volume was 1.0 μl. The chromatogram gave the following response of methylene chloride at 1.77 min., norbornadiene at 2.65 min., *exo*-5-chloronorborene at 8.22 min. and 3-chloronortricylene at 10.41 min.

Analysis of Products by GC/MS. All spectra were obtained on a Hewlett Packard 5995 gas chromatography / mass spectrometer with HP-5 column (30 m x 0.25 mm, 0.25 μm film thickness, part no. 19091J-433), using the parameters indicated for gas chromatographic analysis.

Synthesis of *exo*-5-Chloronorbornene and 3-Chloronortricyclene Mixture. A charge of 250 ml of methylene chloride containing 4.618 g (~0.05 mole) of norbornadiene was added to a 500 ml three neck round-bottomed flask containing 30.047 g of silica gel. The silica gel had been pretreated at 120 °C for at least 48 hours and

cooled to room temperature under N_2. The mixture in the flask was stirred with a magnetic stirrer at room temperature. The reaction started when 11.9g (~0.10 mole) of thionyl chloride was added to the flask. The reaction was carried out under N_2 for one hour and the methylene chloride solution was prepared according to the **Standard Preparative-Scale Reaction** procedure. A mixture of 69.9% exo-5-chloronorborene, 30.1% 3-chloronortricylene and 16.8% unreacted norbornadiene was detected and analyzed by gas chromatography. This mixture weighed 1.501g (28.8% yield, or 34.7% net yield, if corrected for unreacted norbornadiene). GC/MS spectra confirmed the formation of these compounds.

Synthesis of *exo,exo*-6-Chlorobicyclo[2.2.1]hept-2-ene-5-d, *exo,anti*-5-Chlorobicyclo[2.2.1]hept-2-ene-7-d and 5-Chlorotricyclo[2.2.1.$0^{2,6}$]heptane-3-d, *exo*-5-Chloronorbornene and 3-Chloronotricyclene Mixture with Deuterated Alumina. Approximately 20g of aluminum oxide, deuterated (Aldrich, cat. No. 36,347-2) was placed into a test tube sealed with high purity N_2 in a drying pistol. The deuterated alumina was equilibrated at nearly120 °C in a drying pistol heated by refluxing 3-pentanol (b.p.114-116 °C). After 48 hours, 15.031g of so-treated deuterated alumina was combined with 2.305g of norbornadiene and 125 ml of methylene chloride, which was previously distilled from calcium chloride.[18] The reaction was carried out under high purity N_2 when 5.948g of thionyl chloride was added into the stirred solution. The reaction was stopped at one hour and the methylene chloride solution was prepared using the same procedure described in the **Standard Preparative-Scale Reaction**. This

afforded a 1.728g (33.3 % yield) mixture of 29% *exo,exo*-6-chlorobicyclo[2.2.1]hept-2-ene-5-d, 14% *exo,anti*-5-chlorobicyclo[2.2.1]hept-2-ene-7-d, 19% 5-chlorotricyclo[2.2.1.$0^{2,6}$]heptane-3-d, 27% *exo*-5-chloronorbornene and 11% 3-chloronotricyclene, as per analysis by GC/MS.

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